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The Green–Kubo formula, autocorrelation function and fluctuation spectrum for finite Markov chains with continuous time

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Abstract

A general form of the Green–Kubo formula, which describes the fluctuations pertaining to all the steady states whether equilibrium or non-equilibrium, for a system driven by a finite Markov chain with continuous time (briefly, MC) $\{\xi_t\}$, is shown. The equivalence of different forms of the Green–Kubo formula is exploited. We also look at the differences in terms of the autocorrelation function and the fluctuation spectrum between the equilibrium state and the non-equilibrium steady state. Also, if the MC is in the non-equilibrium steady state, we can always find a complex function φ, such that the fluctuation spectrum of $\{\varphi(\xi_t)\}$ is non-monotonous in $[0, +\infty)$.

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Introduction

The Green–Kubo formula (or, say, Einstein relation), which gives the relation between the 'velocity' and the diffusion coefficient for a diffusion process, has been studied by many authors such as [1, 5–7, 10, 14, 18–20] etc. The well-known form of this formula is the equality

$$\int_0^\infty \langle \tilde{b}^T(\xi_t)\tilde{b}(\xi_0)\rangle \, \mathrm{d}t = \frac{1}{2}\langle \mathrm{tr}\, G(\xi_t)\rangle \tag{1}$$

for a reversible diffusion process $\{\xi_t\}$ in high dimensions with the generator

$$\mathsf{L} = \tfrac{1}{2}\nabla G\nabla + b\nabla, \tag{2}$$

$$b = \tfrac{1}{2}G\nabla \log \rho, \tag{3}$$

where G is the diffusion coefficient, ρ is the stationary distribution and

$$\tilde{b} = b + \tfrac{1}{2}\nabla \cdot G \tag{4}$$

is the mean forward velocity and $\tilde{b}^T$ is its transpose [19].

It is difficult to extend the Green–Kubo formula to the system driven by a MC directly, since in the state space of the MC, there is usually no topology, and the state is not scalar, and so it is not clear what the velocity of the process means. In [20], a real observable process of the system was considered, the velocity and the diffusion coefficient were defined[1] and the Green–Kubo formula was extended to a MC in an equilibrium state. In the present paper, we follow this idea and introduce real observable vector-valued processes, and a more general Green–Kubo formula as (1) is obtained for a finite MC, whether in an equilibrium state or in a non-equilibrium steady state.

There have been different forms for the Green–Kubo formula, and in the discussion section we will show that they are equivalent.

In section 2, based on the same equalities from which we obtain the Green–Kubo formula, the form of autocorrelation function and the fluctuation spectrum of the observable process are exploited. Also, we look at the differences between the equilibrium state and the non-equilibrium steady state in terms of the autocorrelation function and the fluctuation spectrum. We emphasize that some terms may appear in the expressions of the autocorrelation function and the fluctuation spectrum in the case of a non-equilibrium steady state, while they will not appear in the case of an equilibrium state. Also, we find out that the non-equilibrium steady state may result in the non-monotonous fluctuation spectrum in $[0, +\infty)$ for some observable processes.

1. Green–Kubo formula

Let $\{\xi_t : -\infty < t < \infty\}$ be a system driven by a finite n-state Markov chain with the stationary measure $\boldsymbol{\mu}$, the transition probability $\{\mathsf{P}_{ij}(t)\}$ and the transition rate matrix $\mathsf{Q} = (q_{ij})_{n\times n}$. Let $\mathcal{P}_t$ be the σ-algebra of the past of t, generated by $\{\xi_s : s \leqslant t\}$ (the process before time t), and $\mathcal{F}_t$ be the σ-algebra of the future of t, generated by $\{\xi_s : s \geqslant t\}$ (the process after time t). Given a d-dimension vector-valued observable $\varphi = (\varphi_1, \varphi_2, \ldots, \varphi_d)$, for each fixed path ω, it does not make sense to consider the velocity of $\varphi(\xi_t(\omega))$ as usual, since it is either 0 or does not exist on a path. But if we take the average conditioning on the past (future), which means the conditional expectation with respect to $\mathcal{P}_t$ $(\mathcal{F}_t)$, then it should be meaningful. Thus we can define the forward (backward) velocity as follows:

Definition 1.1. *For each $t \in R^1$, if*

$$\mathsf{D}\varphi(\xi_t) = \lim_{\triangle t\downarrow 0} \mathrm{E}\left\{ \frac{\varphi(\xi_{t+\triangle t}) - \varphi(\xi_t)}{\triangle t} \middle| \mathcal{P}_t \right\}$$

and

$$\mathsf{D}_*\varphi(\xi_t) = \lim_{\triangle t\downarrow 0} \mathrm{E}\left\{ \frac{\varphi(\xi_t) - \varphi(\xi_{t-\triangle t})}{\triangle t} \middle| \mathcal{F}_t \right\}$$

exist as limits in $\mathcal{L}^1$, then $\mathsf{D}\varphi(\xi_t)$ and $\mathsf{D}_*\varphi(\xi_t)$ are called the mean forward velocity and the mean backward velocity, respectively.

In an equilibrium state, we always have $\mathsf{D}\varphi(\xi_t) = -\mathsf{D}_*\varphi(\xi_t)$, while for a Markov process in a non-equilibrium steady state, this is not true.

[1] This thought of the observable and the velocity of the observable also appeared in [2].

Definition 1.2. *For any $t \in R^1$, we define the diffusion coefficient matrix for $\{\varphi(\xi_t)\}$ as*

$$\mathsf{G}\varphi(\xi_t) = \lim_{\triangle t \downarrow 0} \mathrm{E}\left\{ \frac{(\varphi(\xi_{t+\triangle t}) - \varphi(\xi_t))^T (\varphi(\xi_{t+\triangle t}) - \varphi(\xi_t))}{\triangle t} \middle| \mathcal{P}_t \right\}, \tag{5}$$

if each element of the matrix exists[2].

$\mathsf{G}\varphi(\xi_t)$ is always a positive defined matrix. Denote its (i, j) entry by $\mathsf{G}_{ij}\varphi(\xi_t)$. Our main theorem of this section is given below.

Theorem 1.3 (Green–Kubo formula)**.** *For a stationary finite Markov chain $\{\xi_t\}$, and a d-dimensional vector-valued observable φ, the following equality holds:*

$$\begin{aligned} \frac{1}{2}\langle \operatorname{tr} \mathsf{G}\varphi(\xi_t)\rangle &= \int_0^{+\infty} \langle (\mathsf{D}\varphi)^T(\xi_0)\mathsf{D}\varphi(\xi_t)\rangle \,\mathrm{d}t = \int_0^{+\infty} \langle (\mathsf{D}_*\varphi)^T(\xi_0)\mathsf{D}_*\varphi(\xi_t)\rangle \,\mathrm{d}t \\ &= -\int_0^{+\infty} \langle (\mathsf{D}_*\varphi)^T(\xi_0)\mathsf{D}\varphi(\xi_t)\rangle \,\mathrm{d}t. \end{aligned} \tag{6}$$

Proof

$$\begin{aligned} &\int_0^{+\infty} \langle (\mathsf{D}\varphi)^T(\xi_0)\mathsf{D}\varphi(\xi_t)\rangle \,\mathrm{d}t \\ &\quad = \lim_{t\to\infty} \langle (\mathsf{D}\varphi)^T(\xi_0)\varphi(\xi_t)\rangle - \langle (\mathsf{D}\varphi)^T(\xi_0)\varphi(\xi_0)\rangle \quad \text{(by proposition 1.7)} \\ &\quad = -\langle (\mathsf{D}\varphi)^T(\xi_0)\varphi(\xi_0)\rangle \quad \text{(by proposition 1.9)} \\ &\quad = \frac{1}{2}\langle \operatorname{tr} \mathsf{G}\varphi(\xi_t)\rangle \quad \text{(by corollary 1.11).} \end{aligned}$$

In the same way, one can obtain the other equalities. □

This theorem can also be written in the following form:

Theorem 1.4.

$$\langle \mathsf{G}_{ij}\varphi(\xi_t)\rangle = \int_{-\infty}^{+\infty} \langle \mathsf{D}\varphi_i(\xi_0)\mathsf{D}\varphi_j(\xi_t)\rangle \,\mathrm{d}t. \tag{7}$$

Proof. Similar to the proof of the expression (6), we have

$$\begin{aligned} &\int_{-\infty}^{+\infty} \langle \mathsf{D}\varphi_i(\xi_0)\mathsf{D}\varphi_j(\xi_t)\rangle \,\mathrm{d}t \\ &\quad = \int_0^{+\infty} \langle \mathsf{D}\varphi_i(\xi_0)\mathsf{D}\varphi_j(\xi_t)\rangle \,\mathrm{d}t + \int_0^{+\infty} \langle \mathsf{D}\varphi_j(\xi_0)\mathsf{D}\varphi_i(\xi_t)\rangle \,\mathrm{d}t \\ &\quad = -\langle \varphi_j(\xi_0)\mathsf{D}\varphi_i(\xi_0)\rangle - \langle \varphi_i(\xi_0)\mathsf{D}\varphi_j(\xi_0)\rangle \\ &\quad = \langle \mathsf{G}_{ij}\varphi(\xi_t)\rangle \quad \text{(by proposition 1.10).} \end{aligned}$$

□

Remark 1. The equality (7) is the original type of the Green–Kubo formula given by Kubo [14] under the condition that the equality (3) (i.e. Onsager's postulate) holds. In fact, (7) implies (6).

[2] [16] gave these types of mean velocities and mean diffusion coefficient for stochastic processes but did not consider the observable, and these definitions were used in many books such as [2, 9] etc.

1.1. Proof of the Green–Kubo formula

This subsection contains some pure mathematical lemmas, and those readers who wish may omit them.

For the finite MC, the backward equation and the forward equation can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathsf{P}(t) = \mathsf{QP}(t) = \mathsf{P}(t)\mathsf{Q}, \tag{8}$$

where Q is the transition rate matrix, and $\mathsf{P}(t)$ is the transition probability of the process.

Notation 1. *Let the row vector* $\boldsymbol{\mu} = (\mu_1, \mu_2, \ldots, \mu_n)$ *be the stationary distribution of the MC. Let*

$$\nu_i = \begin{cases} 0 & \text{when } \mu_i = 0, \\ \dfrac{1}{\mu_i} & \text{when } \mu_i \neq 0. \end{cases}$$

Define the diagonal matrix $\mathsf{U} = \mathrm{diag}(\mu_1, \mu_2, \ldots, \mu_n)$*, the diagonal matrix* $\mathsf{V} = \mathrm{diag}(\nu_1, \nu_2, \ldots, \nu_n)$*, and matrix* $\tilde{\mathsf{Q}} = \mathsf{VQ}^T\mathsf{U}$ *where* Q^T *is the transpose matrix of* Q.

Remark 2. For the stationary MC $\{\xi_t\}$, since the probability of $\{\xi_t\}$ being in the transient states is zero, and all the recurrent states can be divided into some communicating recurrent classes, without loss of generality we assume that $\{\xi_t\}$ has only one communicating recurrent class and has no transient state in the proof parts of the present paper. But our conclusions are all valid for any stationary MC.

Notation 2. $\langle\cdot\rangle$ *stands for the ensemble average.*

Notation 3. *In this subsection, we consider the inner product in real linear space* $\mathcal{R}^n(\boldsymbol{\mu})$ *with distribution* $\boldsymbol{\mu}$ *as*

$$\langle f_1, f_2\rangle = \sum_{i=1}^{n} \mu_i f_1(i) f_2(i), \qquad \forall f_1, \quad f_2 \in \mathcal{R}^n.$$

Notation 4. *Denote* $f = (f_1, f_2, \ldots, f_d)$ *and* $g = (g_1, g_2, \ldots, g_d)$*, where* $f_k, g_k \in \mathcal{R}^n, k = 1, 2, \ldots, d$

Lemma 1.5.

$$\mathsf{D}f(x) = \mathsf{Q}f(x) = (\mathsf{Q}f_1(x), \mathsf{Q}f_2(x), \ldots, \mathsf{Q}f_d(x)),$$
$$\mathsf{D}_*g(x) = -\tilde{\mathsf{Q}}g(x) = -(\tilde{\mathsf{Q}}g_1(x), \tilde{\mathsf{Q}}g_2(x), \ldots, \tilde{\mathsf{Q}}g_d(x)).$$

Proof

$$\mathsf{D}f(\xi_t) = \lim_{\triangle t\downarrow 0} \mathrm{E}\left\{\frac{f(\xi_{t+\triangle t}) - f(\xi_t)}{\triangle t}\middle|\mathcal{P}_t\right\}$$
$$= \lim_{\triangle t\downarrow 0} \mathrm{E}\left\{\frac{f(\xi_{t+\triangle t}) - f(\xi_t)}{\triangle t}\middle|\xi_t\right\}, \quad \text{(by the Markov property)}$$

then

$$\mathsf{D}f_k(x) = \lim_{\triangle t\downarrow 0} \mathrm{E}\left\{\frac{f_k(\xi_{t+\triangle t}) - f_k(\xi_t)}{\triangle t}\middle|\xi_t = x\right\}$$
$$= \mathsf{Q}f_k(x). \quad \text{(by the definition of the generator)}$$

In the same way, one can obtain $\mathsf{D}_*g(x)$. □

Proposition 1.6. *When $t \geqslant 0$, we have*

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle f^T(\xi_0)g(\xi_t)\rangle = \langle f^T(\xi_0)\mathsf{D}g(\xi_t)\rangle = -\langle(\mathsf{D}_* f)^T(\xi_0)g(\xi_t)\rangle. \tag{9}$$

Proof. When $t \geqslant 0$, we have

$$\begin{aligned}\langle f^T(\xi_0)g(\xi_t)\rangle &= \sum_{k=1}^{d}\langle f_k(\xi_0)g_k(\xi_t)\rangle \\ &= \sum_{k=1}^{d}\sum_{i,j=1}^{n}\mu_i f_k(i)\mathsf{P}_{ij}(t)g_k(j) \\ &= \sum_{k=1}^{d}\langle \mathsf{P}(t)g_k, f_k\rangle.\end{aligned}$$

Then

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\langle f^T(\xi_0)g(\xi_t)\rangle &= \frac{\mathrm{d}}{\mathrm{d}t}\sum_{k=1}^{d}\langle \mathsf{P}(t)g_k, f_k\rangle \\ &= \sum_{k=1}^{d}\langle \mathsf{P}(t)\mathsf{Q}g_k, f_k\rangle = \sum_{k=1}^{d}\langle \mathsf{Q}\mathsf{P}(t)g_k, f_k\rangle \\ &= \sum_{k=1}^{d}\langle \mathsf{P}(t)\mathsf{Q}g_k, f_k\rangle = \sum_{k=1}^{d}\langle \mathsf{P}(t)g_k, \tilde{\mathsf{Q}}f_k\rangle \\ &= \langle f^T(\xi_0)\mathsf{D}g(\xi_t)\rangle = -\langle(\mathsf{D}_* f)^T(\xi_0)g(\xi_t)\rangle.\end{aligned}$$

□

Proposition 1.7.

$$\begin{aligned}\int_0^{+\infty}\langle f^T(\xi_0)\mathsf{D}g(\xi_t)\rangle\,\mathrm{d}t &= -\int_0^{+\infty}\langle(\mathsf{D}_* f)^T(\xi_0)g(\xi_t)\rangle\,\mathrm{d}t \\ &= \lim_{t\to+\infty}\langle f^T(\xi_0)g(\xi_t)\rangle - \langle f^T(\xi_0)g(\xi_0)\rangle.\end{aligned}$$

Proof. Integrate the expression (9) directly. □

Lemma 1.8. *Let* $\mathsf{W} = \lim_{t\to\infty}\mathsf{P}(t)$. *Then* $\mathsf{W}\mathsf{Q} = \mathsf{W}\tilde{\mathsf{Q}} = \tilde{\mathsf{Q}}\mathsf{W} = 0$.

Proof. The equality $\mathsf{W}\mathsf{Q} = 0$ can be obtained directly from the equality $\mathsf{W}\mathsf{P}(t) = \mathsf{W}$ which is in [3, p 184], [4, p237]. Since the stationary MC $\{\xi_t\}$ has only one communicating recurrent class and has no transient state, $\mathsf{W} = \mathrm{I}\boldsymbol{\mu}$, where vector $\mathrm{I} = (1, 1, \ldots, 1)^T$. Since $\boldsymbol{\mu}\tilde{\mathsf{Q}} = \tilde{\mathsf{Q}}\mathrm{I} = 0$, $\mathsf{W}\tilde{\mathsf{Q}} = \mathrm{I}\boldsymbol{\mu}\tilde{\mathsf{Q}} = 0$, and $\tilde{\mathsf{Q}}\mathsf{W} = \tilde{\mathsf{Q}}\mathrm{I}\boldsymbol{\mu} = 0$. □

Proposition 1.9.

$$\lim_{t\to+\infty}\langle(\mathsf{D}f)^T(\xi_0)g(\xi_t)\rangle = \lim_{t\to+\infty}\langle f^T(\xi_0)\mathsf{D}g(\xi_t)\rangle = \lim_{t\to+\infty}\langle f^T(\xi_0)\mathsf{D}_* g(\xi_t)\rangle = 0.$$

Proof

$$\begin{aligned}\lim_{t\to+\infty}\langle f^T(\xi_0)\mathsf{D}g(\xi_t)\rangle &= \lim_{t\to+\infty}\sum_{k=1}^{d}\langle \mathsf{P}(t)\mathsf{Q}g_k, f_k\rangle \\ &= \sum_{k=1}^{d}\langle \mathsf{W}\mathsf{Q}g_k, f_k\rangle \\ &= 0. \quad \text{(by lemma 1.8)}\end{aligned}$$

Similarly, one can obtain $\lim_{t\to+\infty}\langle(\mathsf{D}f)^T(\xi_0)g(\xi_t)\rangle = \lim_{t\to+\infty}\langle f^T(\xi_0)\mathsf{D}_*g(\xi_t)\rangle = 0.$ □

Proposition 1.10.

$$\langle \mathsf{G}_{ij}\varphi(\xi_t)\rangle = -\langle\varphi_j(\xi_0)\mathsf{D}\varphi_i(\xi_0)\rangle - \langle\varphi_i(\xi_0)\mathsf{D}\varphi_j(\xi_0)\rangle. \tag{10}$$

Proof

$$\begin{aligned}\langle \mathsf{G}_{ij}\varphi(\xi_t)\rangle &= \lim_{\triangle t\downarrow 0}\mathrm{E}\left\{\frac{1}{\Delta t}\mathrm{E}\{[\varphi_i(\xi_{t+\triangle t})-\varphi_i(\xi_t)][\varphi_j(\xi_{t+\triangle t})-\varphi_j(\xi_t)]|\mathcal{P}_t\}\right\}\\ &= \lim_{\triangle t\downarrow 0}\frac{1}{\Delta t}\mathrm{E}\{[\varphi_i(\xi_{t+\triangle t})-\varphi_i(\xi_t)][\varphi_j(\xi_{t+\triangle t})-\varphi_j(\xi_t)]\}\\ &= \lim_{\triangle t\downarrow 0}\frac{1}{\Delta t}\mathrm{E}\{2\varphi_i(\xi_t)\varphi_j(\xi_t)-\varphi_i(\xi_{t+\triangle t})\varphi_j(\xi_t)-\varphi_j(\xi_{t+\triangle t})\varphi_i(\xi_t)\}\\ &= \lim_{\triangle t\downarrow 0}\frac{1}{\Delta t}[\langle\varphi_i,\varphi_j\rangle - \langle\mathsf{P}(\Delta t)\varphi_i,\varphi_j\rangle] + \lim_{\triangle t\downarrow 0}\frac{1}{\Delta t}[\langle\varphi_j,\varphi_i\rangle - \langle\mathsf{P}(\Delta t)\varphi_j,\varphi_i\rangle]\\ &= \left\langle\lim_{\triangle t\downarrow 0}\frac{\mathsf{I}-\mathsf{P}(\Delta t)}{\Delta t}\varphi_i,\varphi_j\right\rangle + \left\langle\lim_{\triangle t\downarrow 0}\frac{\mathsf{I}-\mathsf{P}(\Delta t)}{\Delta t}\varphi_j,\varphi_i\right\rangle\\ &= -\langle\mathsf{Q}\varphi_i,\varphi_j\rangle - \langle\mathsf{Q}\varphi_j,\varphi_i\rangle\\ &= -\langle\varphi_j(\xi_0)\mathsf{D}\varphi_i(\xi_0)\rangle - \langle\varphi_i(\xi_0)\mathsf{D}\varphi_j(\xi_0)\rangle,\end{aligned}$$

where I is the $n\times n$ unit matrix. □

Corollary 1.11.

$$\langle \mathrm{tr}\,\mathsf{G}\varphi(\xi_t)\rangle = -2\langle(\mathsf{D}\varphi)^T(\xi_0)\varphi(\xi_0)\rangle. \tag{11}$$

Proof. It can be obtained directly by proposition 1.10. □

2. The autocorrelation function and the fluctuation spectrum

In this section, for simplicity we prefer to consider the scalar-valued observable. And because the irreversibility cannot be seen in autocorrelation function of only real number observable, we consider a complex number value observable.

Notation 5. *It is well known that there exists a non-singular* $n\times n$ *matrix* F *such that* $\mathsf{Q}=\mathsf{F}JF^{-1}$*, where* J *is its Jordan normal form. Since 0 is the single eigenvalue of the generator* Q *corresponding to the eigenvector* $\boldsymbol{f}_1=(1,1,\ldots,1)^T$*, we might as well denote that* $\mathsf{F}=(\boldsymbol{f}_1,\boldsymbol{f}_2,\ldots,\boldsymbol{f}_n)$*. Then for any vector* $\varphi\in\mathcal{C}^n$*, it can be decomposed as the linear combination of* $\boldsymbol{f}_j$*,* $j=1,2,\ldots,n$*, i.e.* $\varphi=\sum_{j=1}^n b_j\boldsymbol{f}_j$*.*

Notation 6. *Suppose the Jordan normal form* $\mathsf{J}=\mathrm{diag}(\mathsf{J}_1,\mathsf{J}_2,\ldots,\mathsf{J}_\gamma)$*, where* J_k *is a* $p_k\times p_k$ *Jordan block with diagonal entry* $-\lambda_k$ *and* $k=1,2,\ldots,\gamma$*. It is easy to know that* $\lambda_1=0$ *and* J_1 *degenerates to a* 1×1 *Jordan block.*

Let us calculate the autocorrelation function and the fluctuation spectrum of the observable process $\{\varphi(\xi_t)\}$.

Theorem 2.1. *The autocorrelation function of* $\{\varphi(\xi_t)\}$ *is*

$$B_\varphi(t) = \sum_{k=2}^{\gamma}\sum_{l=0}^{p_k-1}C_{k,l}\frac{t^l}{l!}\exp(-\lambda_k t) \qquad when \quad t\geqslant 0, \tag{12}$$

where $C_{k,l}$ is a complex constant independent of t. Especially, if the MC $\{\xi_t\}$ is in an equilibrium state, then the autocorrelation function is

$$B_\varphi(t) = \sum_{k=2}^{\gamma} c_k \exp\{-\lambda_k |t|\}, \tag{13}$$

where c_k is a positive constant independent of t.

Proof. If $\boldsymbol{f}_i = \boldsymbol{g}_s$, where $1 \leqslant s \leqslant p_k$, and $\{\boldsymbol{g}_1, \boldsymbol{g}_2, \ldots, \boldsymbol{g}_{p_k}\}$ is a cycle of generalized eigenvectors of Q corresponding to $-\lambda_k$, then

$$\mathsf{P}_t \boldsymbol{f}_i = \sum_{l=0}^{s-1} \frac{t^l}{l!} \exp(-\lambda_k t) \boldsymbol{g}_{s-l},$$

and

$$\begin{aligned} \langle \mathsf{P}_t \boldsymbol{f}_i, \varphi \rangle &= \sum_{l=0}^{s-1} \frac{t^l}{l!} \exp(-\lambda_k t) \langle \boldsymbol{g}_{s-l}, \varphi \rangle \\ &= \sum_{l=0}^{s-1} \tilde{C}_l \frac{t^l}{l!} \exp(-\lambda_k t), \end{aligned}$$

where $\tilde{C}_l$ is a constant independent of t. By lemma 2.6, when $t \geqslant 0$:

$$B_\varphi(t) = \sum_{i=2}^{n} b_i \langle \mathsf{P}_t \boldsymbol{f}_i, \varphi \rangle. \tag{14}$$

Combine the coefficients of $\left\{\frac{t^l}{l!} \exp(-\lambda_k t)\right\}$ in the right-hand side of (14). One can obtain that $B_\varphi(t)$ is the complex linear combination of $\left\{\frac{t^l}{l!} \exp(-\lambda_k t)\right\}$, where $l = 0, 1, 2, \ldots, p_k - 1$ and $k = 2, 3, \ldots, \gamma$. Then the expression (12) is proved.

In particular, if the MC $\{\xi_t\}$ is in the equilibrium state, by lemma 2.4 we can obtain the expression (13) (please refer to [13, p 120], [20] for detail). □

Remark 3. Let $-a_k + \mathrm{i}\omega_k$ be the complex eigenvalue of the Q. Then the terms $\left\{\frac{|t|^l}{l!} \exp\{-a_k|t|\} \cos(\omega_k t), \mathrm{i}\frac{|t|^l}{l!} \exp\{-a_k|t|\} \sin(\omega_k t) : l \geqslant 1 \text{ or } \omega_k \neq 0\right\}$ [3] may appear in the autocorrelation function in the case of a non-equilibrium steady state, while they will not appear in the case of an equilibrium state.

Theorem 2.2. *The fluctuation spectrum of $\{\varphi(\xi_t)\}$ is the real linear combination of $\left\{\frac{a_k}{[(\lambda-\omega_k)^2+a_k^2]^l}, \frac{\lambda-\omega_k}{[(\lambda-\omega_k)^2+a_k^2]^l} : l = 1, 2, \ldots, p_k, k = 2, 3, \ldots, \gamma\right\}$, where $-a_k + \mathrm{i}\omega_k$ is the eigenvalue of the Q. Especially, if the MC $\{\xi_t\}$ is in an equilibrium state, then the fluctuation spectrum is the positive linear combination of the $\left\{\frac{a_k}{\lambda^2+a_k^2}\right\}$.*

Proof. Since

$$\int_0^{+\infty} \frac{t^l}{l!} \exp(-\lambda_k t) \cdot \exp(-\mathrm{i}\lambda t)\, \mathrm{d}t = \frac{1}{(\mathrm{i}\lambda + \lambda_k)^{l+1}},$$

one can obtain

$$\begin{aligned} &\frac{1}{2} \int_{-\infty}^{+\infty} \frac{|t|^l}{l!} (c \cdot \exp(-\lambda_k t) \chi_{[0,+\infty)}(t) + c^* \cdot \exp(\lambda_k^* t) \chi_{(-\infty,0)}(t)) \cdot \exp(-\mathrm{i}\lambda t)\, \mathrm{d}t \\ &\quad = \mathrm{Re}\left[\frac{c}{(\mathrm{i}\lambda + \lambda_k)^{l+1}}\right], \end{aligned}$$

[3] In the present paper, denote $\mathrm{i} = \sqrt{-1}$.

where $l = 0, 1, 2, \ldots, p_k - 1$; and c^*, λ_k^* are the complex conjugates of the c, λ_k respectively, and $\chi_{[0,+\infty)}(t)$, $\chi_{(-\infty,0)}(t)$ are the characteristic functions of the set $[0, +\infty)$ and the set $(-\infty, 0)$, respectively. The real part of $\frac{c}{(\mathrm{i}\lambda+\lambda_k)^l}$ is just the linear combination

$$\left\{ \frac{a_k}{\left[(\lambda - \omega_k)^2 + a_k^2\right]^l}, \frac{\lambda - \omega_k}{\left[(\lambda - \omega_k)^2 + a_k^2\right]^l} \right\}.$$

Then by theorem 2.1, one knows that this theorem is true.

In particular, when all the eigenvalues degenerate to real number, i.e. $\omega_k = 0$, we can obtain that the fluctuation spectrum degenerates to the real linear combination of

$$\left\{ \frac{a_k}{\left(\lambda^2 + a_k^2\right)^l}, \frac{\lambda}{\left(\lambda^2 + a_k^2\right)^l} \right\}.$$

For the equilibrium state, please refer to [13, p 120], [20] for detail. □

Remark 4. The terms

$$\left\{ \frac{a_k}{\left[(\lambda - \omega_k)^2 + a_k^2\right]^l}, \frac{\lambda - \omega_k}{\left[(\lambda - \omega_k)^2 + a_k^2\right]^l} : \omega_k \neq 0 \text{ or } l \geqslant 2 \right\}$$

may appear in the fluctuation spectrum in the case of a non-equilibrium steady state, while they will not appear in the case of an equilibrium state.

Theorem 2.3. *For any finite MC* $\{\xi_t\}$*, if it is in a non-equilibrium steady state, then there exists* $\varphi \in C^n$ *such that the fluctuation spectrum of* $\{\varphi(\xi_t)\}$ *is non-monotonous in* $[0, +\infty)$.

Proof. If the MC is in a non-equilibrium steady state, then the eigenvalues of Q appear in one of the following three cases by lemma 2.4.

(1) There exists a complex eigenvalue $-a + \mathrm{i}\omega$ corresponding to the normalized eigenvector φ such that $a > 0$, $\omega > 0$.
(2) There exist two distinct nonzero real eigenvalues corresponding to two real eigenvectors φ_1, φ_2, respectively such that $\langle \varphi_1, \varphi_2 \rangle \neq 0$.
(3) Q cannot be diagonalizable. Then there exist $\boldsymbol{g_1}, \boldsymbol{g_2}$ which are generalized eigenvectors of Q corresponding to the real number $-\lambda_k$, such that $\mathsf{Q}\boldsymbol{g_1} = -\lambda_k \boldsymbol{g_1}$, $\mathsf{Q}\boldsymbol{g_2} = \boldsymbol{g_1} - \lambda_k \boldsymbol{g_2}$ and $\langle \boldsymbol{g_1}, \boldsymbol{g_1} \rangle = 1$.

For each case, one special observable φ is constructed such that the fluctuation spectrum is non-monotonous in $[0, +\infty)$ by propositions 2.8, 2.9 and 2.10, respectively. □

Remark 5. In the case of the equilibrium state, one knows that the fluctuation spectrum of any $\{\varphi(\xi_t)\}$ is monotonous in $[0, +\infty)$. Please refer to [13, p 121], [20] for detail.

2.1. Proof of the lemma and the theorem

Notation 7. *In this subsection, we consider the inner product in the complex linear space* $\mathcal{C}^n(\boldsymbol{\mu})$ *with stationary distribution* $\boldsymbol{\mu}$ *as*

$$\langle \boldsymbol{g}_1, \boldsymbol{g}_2 \rangle = \sum_{k=1}^{n} \mu_k g_1(k) g_2^*(k), \qquad \forall \boldsymbol{g_1}, \quad \boldsymbol{g_2} \in \mathcal{C}^n,$$

where $g_2^*(k)$ *stands for the conjugate complex number of* $g_2(k)$.

Lemma 2.4. *The finite MC is in equilibrium, iff all the eigenvalues of* Q *are real, all the eigenspaces of* Q *are orthogonal, and* Q *can be diagonalizable.*

Proof. The sufficiency is a simple linear algebra conclusion and is too mathematical to be worth writing the proof here, so we ignore it.

The necessity is trivial since Q is a self-adjoint operator in the Hilbert space $L^2(\mathcal{C}^n, \mu)$. □

Lemma 2.5.

$$\langle \boldsymbol{f_1}, \boldsymbol{f_k} \rangle = \begin{cases} 1 & \text{when } k = 1; \\ 0 & \text{when } k \neq 1. \end{cases}$$

Proof. If $-\lambda_k$ is the eigenvalue of Q corresponding to the eigenvector $\boldsymbol{f_k}$, $\mathsf{Q}\boldsymbol{f}_k = -\lambda_k \boldsymbol{f}_k$. And

$$\begin{aligned} -\lambda_k \langle \boldsymbol{f_k}, \boldsymbol{f_1} \rangle &= \langle \mathsf{Q}\boldsymbol{f_k}, \boldsymbol{f_1} \rangle \\ &= \sum_{j=1}^{n} f_k(j) \sum_{i=1}^{n} \mu_i q_{ij} \\ &= 0 \quad (\text{since } \boldsymbol{\mu}\mathsf{Q} = 0). \end{aligned}$$

Since $\lambda_k \neq 0$ when $k \neq 1$, $\langle \boldsymbol{f_1}, \boldsymbol{f_k} \rangle = 0$.

Suppose $\{\boldsymbol{g}_1, \boldsymbol{g}_2, \ldots, \boldsymbol{g}_{p_j}\}$ is a cycle of generalized eigenvectors of Q corresponding to $-\lambda_j$. If $\boldsymbol{f}_k = \boldsymbol{g_l}$ where $1 \leqslant l \leqslant p_j$. Then $\mathsf{Q}\boldsymbol{g_l} = \boldsymbol{g_{l-1}} - \lambda_j \boldsymbol{g_l}$, $l = 2, 3, \ldots, p_j$; and $\mathsf{Q}\boldsymbol{g_1} = -\lambda_j \boldsymbol{g_1}$. We know $\langle \boldsymbol{f_1}, \boldsymbol{g_1} \rangle = 0$, and $\langle \mathsf{Q}\boldsymbol{g_l}, \boldsymbol{f_1} \rangle = 0$, $l = 2, 3, \ldots, p_j$. Then

$$\begin{aligned} -\lambda_j \langle \boldsymbol{g_l}, \boldsymbol{f_1} \rangle &= \langle \mathsf{Q}\boldsymbol{g_l} - \boldsymbol{g_{l-1}}, \boldsymbol{f_1} \rangle \\ &= \langle \mathsf{Q}\boldsymbol{g_l}, \boldsymbol{f_1} \rangle - \langle \boldsymbol{g_{l-1}}, \boldsymbol{f_1} \rangle \\ &= -\langle \boldsymbol{g_{l-1}}, \boldsymbol{f_1} \rangle. \end{aligned}$$

By induction, we have $\langle \boldsymbol{f_1}, \boldsymbol{g_l} \rangle = 0$, for $l = 1, 2, 3, \ldots, p_j$. In conclusion, when $k \neq 1$, $\langle \boldsymbol{f_1}, \boldsymbol{f_k} \rangle = 0$ is true. And $\langle \boldsymbol{f_1}, \boldsymbol{f_1} \rangle = 1$ is trivial. Then the lemma is true. □

Lemma 2.6. $\forall t \geqslant 0$,

$$B_\varphi(t) = \sum_{i=2}^{n} b_i \langle \mathsf{P}(t)\boldsymbol{f}_i, \varphi \rangle.$$

Proof

$$\begin{aligned} B_\varphi(t) &= \langle \varphi(\xi_0)^* \varphi(\xi_t) \rangle - |\langle \varphi(\xi_0) \rangle|^2 \\ &= \sum_{i=1}^{n} \mu_i \varphi_i^* \sum_{j=1}^{n} \mathsf{P}_{ij}(t) \varphi_j - \left| \sum_{i=1}^{n} \mu_i \varphi_i \right|^2 \\ &= \langle \mathsf{P}(t)\varphi, \varphi \rangle - |\langle \varphi, \boldsymbol{f}_1 \rangle|^2, \end{aligned}$$

where $\varphi(\xi_0)^*$, φ_i^* are the conjugate complex numbers of $\varphi(\xi_0)$ and φ_i. Since $\varphi = \sum_{i=1}^{n} b_i \boldsymbol{f}_i$, one can get $\langle \varphi, \boldsymbol{f}_1 \rangle = b_1$ by lemma 2.5. And since $\mathsf{P}(t)\boldsymbol{f}_1 = \boldsymbol{f}_1$, one can get $\langle \mathsf{P}(t)\boldsymbol{f}_1, \varphi \rangle = b_1^*$ by lemma 2.5. Thus

$$\begin{aligned} B_\varphi(t) &= \sum_{i=1}^{n} b_i \langle \mathsf{P}(t)\boldsymbol{f}_i, \varphi \rangle - |b_1|^2 \\ &= \sum_{i=2}^{n} b_i \langle \mathsf{P}(t)\boldsymbol{f}_i, \varphi \rangle. \end{aligned}$$

□

Lemma 2.7. *If* $-\lambda_{n_1}, -\lambda_{n_2}, \cdots, -\lambda_{n_k}$ *are the distinct nonzero eigenvalues of* Q *corresponding to the normalized eigenvectors* $\boldsymbol{f}_{n_1}, \boldsymbol{f}_{n_2}, \ldots, \boldsymbol{f}_{n_k}$ *respectively, and* $\psi = \sum_{j=1}^{k} b_{n_j} \boldsymbol{f}_{n_j}$, *then the equality*

$$\frac{1}{2}\int_{-\infty}^{+\infty} B_\psi(t)\exp(-\mathrm{i}\lambda t)\,\mathrm{d}t = \sum_{j=1}^{k} \mathrm{Re}\big[b_{n_j}\langle f_{n_j}, \psi\rangle\big]\frac{a_{n_j}}{\left(\lambda+\omega_{n_j}\right)^2 + a_{n_j}^2} + \sum_{j=1}^{k}\mathrm{Im}\big[b_{n_j}\langle f_{n_j}, \psi\rangle\big]\frac{\lambda+\omega_{n_j}}{\left(\lambda+\omega_{n_j}\right)^2 + a_{n_j}^2} \tag{15}$$

holds, where $\lambda_{n_j} = a_{n_j} + \mathrm{i}\omega_{n_j}, a_{n_j} \neq 0, j = 1, 2, \ldots, k$.

Proof. When $t \geqslant 0$,

$$\mathsf{P}_t \boldsymbol{f}_{n_j} = \exp\left(-\lambda_{n_j} t\right)\boldsymbol{f}_{n_j},$$

then by lemma 2.6,

$$B_\psi(t) = \sum_{j=1}^{k} b_{n_j}\langle \mathsf{P}(t)\boldsymbol{f}_{n_j}, \psi\rangle = \sum_{j=1}^{k} b_{n_j}\langle \boldsymbol{f}_{n_j}, \psi\rangle \exp\{-\lambda_{n_j} t\}.$$

Thus the expression (15) can be obtained directly. □

Proposition 2.8. *If* $-a + \mathrm{i}\omega$ *is a eigenvalue of* Q *corresponding to the normalized eigenvector* φ *where* $\omega > 0, a > 0$, *then the fluctuation spectrum*[4] *of* $\{\varphi(\xi_t)\}$ *is*

$$\frac{a}{(\lambda-\omega)^2 + a^2} = \frac{1}{2}\int_{-\infty}^{+\infty} B_\varphi(t)\exp(-\mathrm{i}\lambda t)\,\mathrm{d}t. \tag{16}$$

Proof. It is the directed corollary of lemma 2.7. □

Proposition 2.9. *When* $-\lambda_k, -\lambda_j$ *are two distinct nonzero real eigenvalues corresponding to two normalized eigenvectors* $\boldsymbol{\varphi_1}, \boldsymbol{\varphi_2}$ *respectively such that* $\langle \boldsymbol{\varphi_1}, \boldsymbol{\varphi_2}\rangle \neq 0$. *Denote* $b = \langle \boldsymbol{\varphi_1}, \boldsymbol{\varphi_2}\rangle(\lambda_j - \lambda_k)$, *and let* $\varphi = \boldsymbol{\varphi_1} - \mathrm{i}\cdot\mathrm{sgn}(b)\boldsymbol{\varphi_2}$ *where* $sgn(\cdot)$ *is the sign function, then the fluctuation spectrum of* $\{\varphi(\xi_t)\}$ *is*

$$\frac{\lambda_k}{\lambda^2+\lambda_k^2} + \frac{\lambda_j}{\lambda^2+\lambda_j^2} + |b|\frac{\lambda(\lambda_k+\lambda_j)}{\left(\lambda^2+\lambda_k^2\right)\left(\lambda^2+\lambda_j^2\right)}.$$

Proof. It is the directed corollary of lemma 2.7. □

Proposition 2.10. *If* $\mathsf{Q}\boldsymbol{g_1} = -\lambda_k \boldsymbol{g_1}, \mathsf{Q}\boldsymbol{g_2} = \boldsymbol{g_1} - \lambda_k \boldsymbol{g_2}$ *where* $-\lambda_k$ *is a real number, and* $\langle \boldsymbol{g_1}, \boldsymbol{g_1}\rangle = 1$. *Let* $\varphi = \boldsymbol{g_1} + \mathrm{i}\boldsymbol{g_2}$, *then the fluctuation spectrum of* $\{\varphi(\xi_t)\}$ *is*

$$\left(1 + \langle \boldsymbol{g_2}, \boldsymbol{g_2}\rangle - \frac{\langle \boldsymbol{g_1}, \boldsymbol{g_2}\rangle}{\lambda_k}\right)\frac{\lambda_k}{\lambda_k^2+\lambda^2} + \langle \boldsymbol{g_1}, \boldsymbol{g_2}\rangle\frac{2\lambda_k^2}{\left(\lambda_k^2+\lambda^2\right)^2} + \frac{2\lambda_k\lambda}{\left(\lambda_k^2+\lambda^2\right)^2}. \tag{17}$$

Proof. When $t \geqslant 0$, $\mathsf{P}(t)\boldsymbol{g_1} = \exp(-\lambda_k t)\boldsymbol{g_1}$, $\mathsf{P}(t)\boldsymbol{g_2} = \exp(-\lambda_k t)(t\boldsymbol{g_1} + \boldsymbol{g_2})$. By theorem 2.1, we can get

$$B_\varphi(t) = (1 + \langle \boldsymbol{g_2}, \boldsymbol{g_2}\rangle + t\langle \boldsymbol{g_1}, \boldsymbol{g_2}\rangle + \mathrm{i}\cdot t)\cdot\exp(-\lambda_k t).$$

[4] About the fluctuation spectrum, we ignore the inessential constant $\frac{1}{\pi}$ in the present paper.

And when $t < 0$,

$$\begin{aligned} B_\varphi(t) &= B_\varphi^*(-t) \\ &= (1 + \langle g_2, g_2\rangle + |t|\langle g_1, g_2\rangle - \mathrm{i}\cdot|t|)\cdot\exp(-\lambda_k|t|). \end{aligned}$$

So

$$B_\varphi(t) = (1 + \langle g_2, g_2\rangle + |t|\langle g_1, g_2\rangle + \mathrm{i}\cdot t)\cdot\exp(-\lambda_k|t|).$$

Then one can obtain the fluctuation spectrum of $\varphi(\xi_t)$ as the expression (17). □

3. Discussion and conclusion

3.1. The Green–Kubo formula

In fact, theorem 1 also shows that the formula in [18]

$$-\int_0^\infty \langle \tilde{b}^T(\xi_t)\tilde{b}_*(\xi_0)\rangle\,\mathrm{d}t = \frac{1}{2}\langle \mathrm{tr}\,G(\xi_t)\rangle \tag{18}$$

is equivalent to (1), since the integral

$$-\int_0^\infty \langle \tilde{b}^T(\xi_t)\tilde{b}_*(\xi_0)\rangle\,\mathrm{d}t = \int_0^\infty \langle \tilde{b}^T(\xi_t)\tilde{b}(\xi_0)\rangle\,\mathrm{d}t,$$

even though their integrands may be different in non-equilibrium systems, where $\tilde{b}_*(\xi_t)$ is the backward velocity.

The extension of the Green–Kubo formula from diffusions to MC is significant. First, one always replaces diffusions by MC in computer simulations since diffusions can be seen as the limits of MC. Secondly, the system in non-equilibrium steady states may appear in some interesting cases. For example in [1, pp 181–186], the motion of a charged test particle in the presence of a constant magnetic field is in a non-equilibrium state.

3.2. The autocorrelation function and fluctuation spectrum

In [11], the differences between the equilibrium state and the non-equilibrium steady state are described in terms of the time reversibility of the processes, self-adjoint property of the generator and the entropy production rate. In this paper, we look at the differences in terms of the autocorrelation function and the fluctuation spectrum.

For the equilibrium state, the autocorrelation function of any observable process $\{\varphi(\xi_t)\}$ is the positive linear combination of $\{\exp\{-\lambda_k|t|\}\}$, and the fluctuation spectrum is the positive linear combination of the functions $\left\{\frac{\lambda_k}{\lambda^2+\lambda_k^2}\right\}$, where $-\lambda_k$ is the eigenvalue of Q. For non-equilibrium steady state, the correlation function is the complex linear combination of $\left\{\frac{|t|^l}{l!}\exp\{-a_k|t|\}\cos(\omega_k t), \mathrm{i}\frac{|t|^l}{l!}\exp\{-a_k|t|\}\sin(\omega_k t) : l \geqslant 0\right\}$, and the fluctuation spectrum is the real linear combination of

$$\left\{\frac{a_k}{\left[(\lambda-\omega_k)^2 + a_k^2\right]^j}, \frac{\lambda-\omega_k}{\left[(\lambda-\omega_k)^2 + a_k^2\right]^j} : j \geqslant 1\right\},$$

where $-a_k + \mathrm{i}\omega_k$ is the eigenvalue of Q.

And if $\{\xi_t\}$ is in a non-equilibrium steady state, we can always find a function φ, such that the fluctuation spectrum of $\{\varphi(\xi_t)\}$ is non-monotonous in $[0, +\infty)$. Therefore one can see why in simulation calculation of stochastic resonance, finding the nonzero peak for the fluctuation spectrum is considered as a criterion of being non-equilibrium [8].

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